

# Laser deposition of ceramics creates high-quality thin films

The technique of using excimer lasers to flash-evaporate ceramic target material provides many advantages over traditional methods.

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**T**he wide range of interesting and useful properties exhibited by ceramics makes them technically important materials. Applications for ceramics range from optics to biomaterials and often require that the material be cast in thin-film form. Ceramic materials are typically made up of several different elements, have a complex unit cell, and have anisotropic physical and chemical properties.

Processing ceramic materials into thin films with conventional coating techniques has been extremely difficult. To counter the difficulties, a novel physical vapor-deposition technique called pulsed laser deposition (PLD) has been developed, using a high-powered excimer laser source to produce high-quality ceramic thin films.<sup>1</sup>

Shortly after the discovery of lasers in the early 1960s, Smith and Turner at the University of Rochester and Bausch & Lomb (Rochester, NY) used a ruby laser to deposit thin films of semiconductors, dielectrics, chalcogenides, and organometallic materials.<sup>2</sup> The transfer of stoichiometry was noted then as an important characteristic of the process. Little further development was pursued until the 1980s, when Cheung and coworkers at Rockwell (Thousand Oaks, CA) used PLD to deposit mercury cadmium telluride thin films for bandgap engineering applications.<sup>3</sup>

With the development of high-temperature superconductivity, PLD development accelerated. Properties such as good film-to-film reproducibility, accurate stoichiometry, single-phase purity, and c-axis orientation were required to exploit the unique properties of high-temperature, superconducting (HTS) thin films. Venkatesan and coworkers (Bellcore, Red Bank, NJ) rediscovered, refined, and popularized PLD to meet these challenges.<sup>4</sup> Since that time, the advantages of PLD for the deposition of ceramic thin films have been successfully applied to many other multicomponent ceramics.

Systems for pulsed laser deposition incorporate a pulsed excimer laser, a simple vacuum chamber, a rotating ceramic

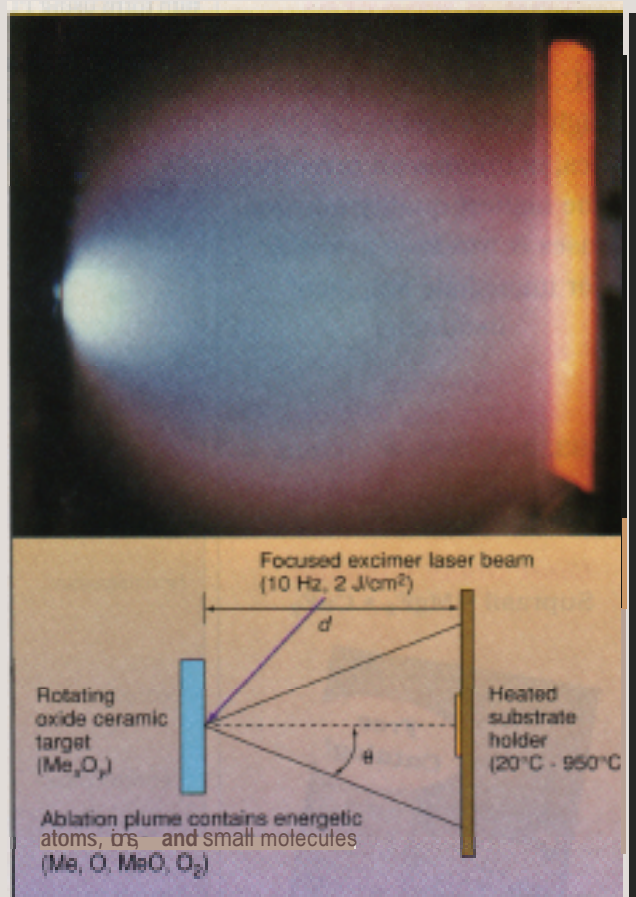


FIGURE 1. Pulsed laser deposition uses a KrF excimer laser to ablate a yttrium barium copper oxide (YBaCu307) target onto a heated magnesium oxide substrate (top). Typical target-substrate distances are approximately 5 cm, and the beam is incident on the rotating target at an angle from the normal (bottom).

target, and a substrate heater. The focused output of the source, typically a short-pulse KrF excimer laser emitting at 248 nm, flash evaporates the target, depositing about one angstrom of material per pulse on the substrate (see Fig. 1). The short penetration depth and rapid heating of the target result in the formation of a highly forward-directed, stoichiometric, and nonthermal plasma plume.

The ability to transfer the stoichiometry of the target pellet to the growing film is a major advantage of the technique. Because there are no filaments or discharges involved, the process also permits deposition in high-pressure, reactive-gas

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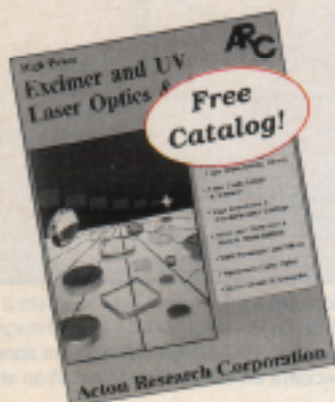
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environments, such as an oxygen environment required for deposition of oxide ceramics. The set-up is simple, and, because the highly focused plume does not coat the rest of the deposition vessel, PLD is environmentally friendly.

The short-pulsed nature of the PLD process yields an instantaneous deposition rate of roughly 1000-10,000 Å/s, four orders of magnitude higher than other continuous techniques. High-temperature superconductors, ferroelectrics, and ferrites can all be deposited in thin-film form using PLD.

### High-temperature superconductors

The discovery that yttrium barium copper oxide (YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub>) became superconducting at high temperatures

brought about renewed interest in the use of superconducting thin films for high-speed, low-power electronic device applications such as compact high-quality-factor filters and Josephson elements for low-power digital computing. Because the electrical transport properties of HTS materials are highly anisotropic and extremely sensitive to the level of oxygen doping, stoichiometric, oriented films were needed to realize the improved electrical performance of HTS. Although similar challenges were present for other electronic ceramics, it was the overwhelming potential of HTS electronics that catalyzed the PLD breakthrough in reproducible ceramic thin-film production (see table).

## Properties and applications of ceramic thin-film materials

Property	Applications	Typical ceramic materials
High T <sub>c</sub> superconductivity	Microwave filters and delay lines, Josephson-junction digital electronics, sensors	YBa <sub>2</sub> Cu <sub>3</sub> O <sub>7</sub> , Tl <sub>2</sub> Ca <sub>2</sub> Sr <sub>2</sub> Cu <sub>3</sub> O <sub>x</sub> , and Nd <sub>1.85</sub> Ce <sub>0.15</sub> CuO <sub>4</sub>
ferroelectricity	DRAM capacitors, NVRAMs, active microwave devices, optoelectronics, MEMS	Pb(Zr,Ti)O <sub>3</sub> , (Sr,Ba)TiO <sub>3</sub> , (Sr,Ba)Nb <sub>2</sub> O <sub>6</sub> , and LiNbO <sub>3</sub>
Ferrimagnetism	Circulators, phase shifters, magnetic recording, patch antennas	BaFe <sub>12</sub> O <sub>19</sub> , Y <sub>3</sub> Fe <sub>5</sub> O <sub>12</sub> , (Mn,Zn)Fe <sub>2</sub> O <sub>4</sub> , and LiFe <sub>2</sub> O <sub>4</sub>
Electrochromic	Optical modulators, sunroofs, sensor protection	WO <sub>3</sub> , MoO <sub>3</sub> , and V <sub>2</sub> O <sub>5</sub>
Electrical-optical	Transparent conductors, oxide conductors, solar-energy management, photovoltaics	F-doped ZnO <sub>2</sub> , In <sub>2</sub> O <sub>3</sub> , and Sn <sub>1-x</sub> Si <sub>x</sub> , (La,Sr)CoO <sub>3</sub>
Thermal and corrosive stability	Oxidation and thermal-protection coatings for turbine blades	Y-ZrO <sub>2</sub> , ZnO <sub>2</sub> , MgAl <sub>2</sub> O <sub>4</sub>
Friction and wear	Hard, low-friction, and wear-resistant coatings	MoS <sub>2</sub> , BN, SiC, and diamond-like carbon
Piezoelectric	Micro-electrical-mechanical (MEMS) machines	Pb(Zr,Ti)O <sub>3</sub>
Giant magnetoresistance	Magnetic recording heads, field sensors	(La,Ca)MnO <sub>3</sub> , Permalloy/Ag multilayers
Biocompatibility	Prosthetic hip/knee implants, sensors	Hydroxylapatite, Al <sub>2</sub> O <sub>3</sub> , TiO <sub>2</sub> , and diamond-like carbon



One of the initial applications of HTS thin films was production of passive microwave devices fabricated from superconducting films deposited onto one side of a dielectric substrate. Due to the extremely low microwave surface resistance intrinsic to superconductors, patterned HTS films reduced conductor losses by orders of magnitude. In applications such as the use of

bandpass filters in communication satellites, the lower conductor losses improve the device performance and reduce the weight enough to justify the added burden of the required cryogenic cooling.

A channelized receiver was fabricated from PLD-deposited  $\text{YBa}_2\text{Cu}_3\text{O}_7$  film deposited on both sides of a  $1 \times 1 \times 0.01$ -in. magnesium oxide substrate (see

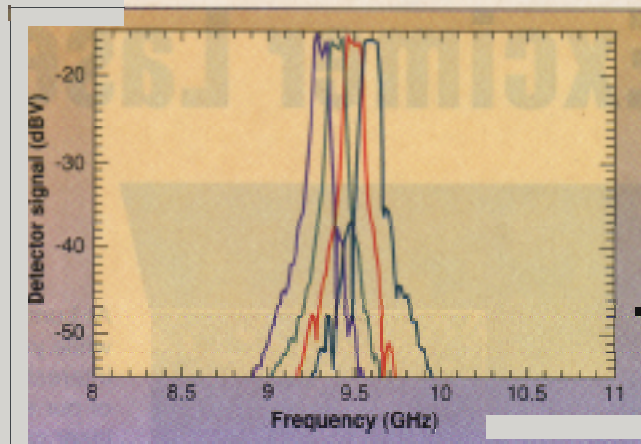


Fig. 2). Fabrication of this type of device initially presented a difficult processing challenge for PLD.

To achieve CAD-predicted performance, HTS films having high spatial uniformity had to be deposited over the 1-in. substrate. The superconducting properties of the film (critical temperature, critical current, penetration depth, and surface resistance) and the crys-

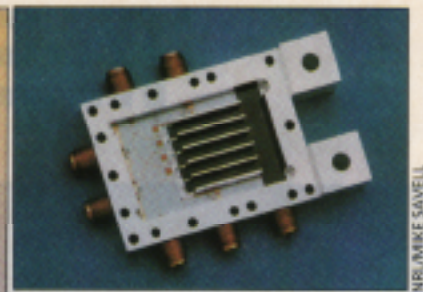
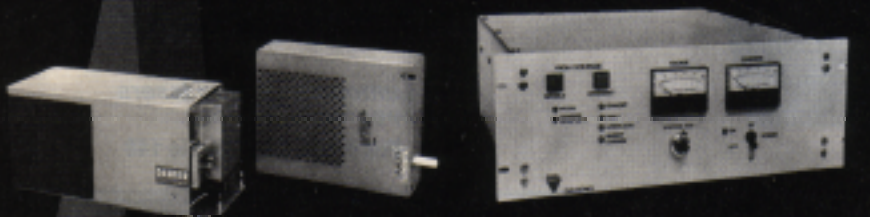


FIGURE 3. Channelized receiver fabricated from PLD-deposited HTS films has very narrow-band-pass characteristics. Each trace represents one channel. Such devices are superior to conventional devices in electrical performance, size, weight, and input power.

talline and structural properties (c-axis orientation, thickness, stoichiometry, surface smoothness) could not vary significantly across the surface, otherwise the internal matching of the individual filters would be compromised.

Because the PLD-produced plume is highly forward-directed, its spatial flux is highly nonuniform and not conducive to the kind of spatial uniformity

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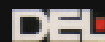
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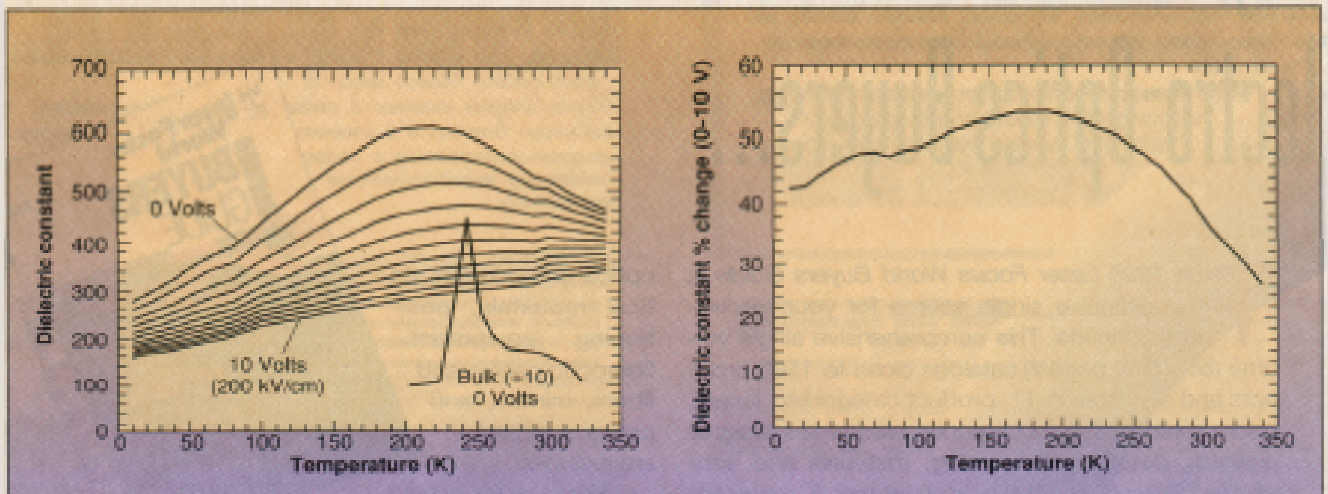
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**FIGURE 3.** The dielectric constant for a  $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{TiO}_3$  ferroelectric thin film for a given applied voltage changes as a function of temperature (left). The peaks of the curves correspond to the Curie temperature for the material. The scaled temperature dependence of bulk  $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{TiO}_3$  for a zero applied field dielectric has a much sharper peak, shifted from that for the thin-film form. These data illustrate the active dielectric property on which an entirely new class of microwave devices will be based. The percent change in the dielectric constant between 0 and 10 V as a function of temperature is more than 50% (right).

primary applications of ferrite thin films are for magnetic recording, for example, as hard disks and recording heads, and

in microwave devices such as circulators, filters, and resonators. Microwave control and signal pro-

cessing functions can be performed using ferrites because these materials have high permeability and resistivity.



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The operation of microwave devices using ferrites depends on the strong coupling of an electromagnetic wave to the individual ferrite magnetic moments as the wave passes through the material. Ferrites display low loss, so the electromagnetic wave undergoes minimum attenuation. These properties make ferrites uniquely suited for microwave applications.

Most commercial ferrite microwave devices currently use bulk single crystal or polycrystalline forms of the material. However, the advent of monolithic microwave integrated circuits (MMICs) has generated renewed interest in development of ferrite thin-film deposition techniques, because bulk ferrite microwave devices constitute a disproportionate amount of the total cost, weight, and size of

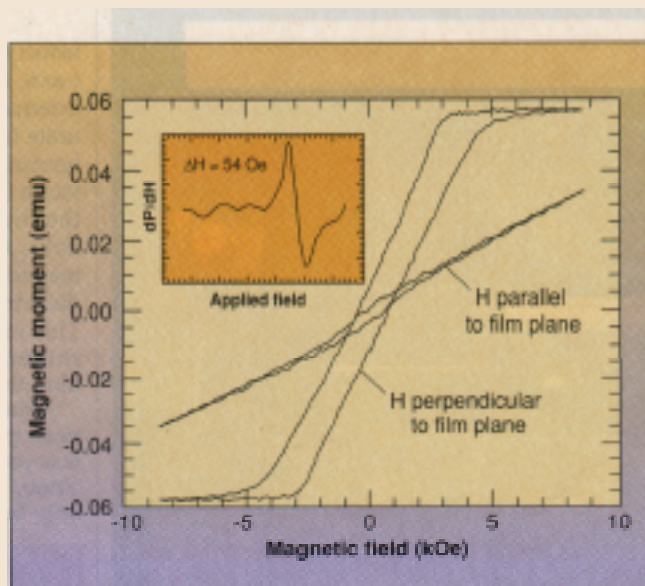


FIGURE 4. Barium ferrite ( $\text{BaFe}_{12}\text{O}_{19}$ ) thin film saturates easily when a magnetic field is applied along the c-axis (easy axis), but requires a large, externally applied magnetic field to saturate in the plane due to the large magnetocrystalline anisotropy field perpendicular to the c-axis (main plots). The ferrimagnetic resonance measured at 85.7 GHz displays a narrow linewidth comparable to the best single-crystal values and indicates small magnetic losses (inset).

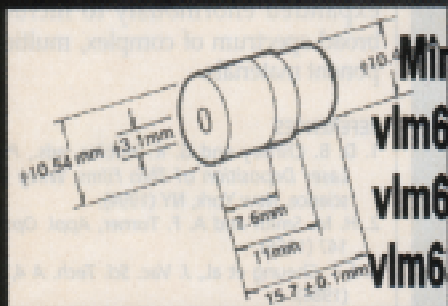
microwave systems. Devices using "thick" ferrite films (approximately 100  $\mu\text{m}$ ) are able to offer considerable advantages over bulk technology in these areas, while demonstrating increased reliability and reproducibility.

Ferrite films grown using PLD have magnetic and structural properties superior to those of films grown using other physical vapor-deposition techniques. The magnetic hysteresis curve for an epitaxial barium ferrite ( $\text{BaFe}_{12}\text{O}_{19}$ ) thin film on (0001) aluminum oxide ( $\text{Al}_2\text{O}_3$ ) indicates that the film is well oriented and has high values for both bulk saturation magnetization ( $4\pi M_s = 4400 \text{ G}$ ) and uniaxial magnetic anisotropy field ( $H_a = 1700 \text{ G}$ ) (see Fig. 4). The film saturates easily when a magnetic field is applied along the c-axis, or easy axis.

Because of the large mag-

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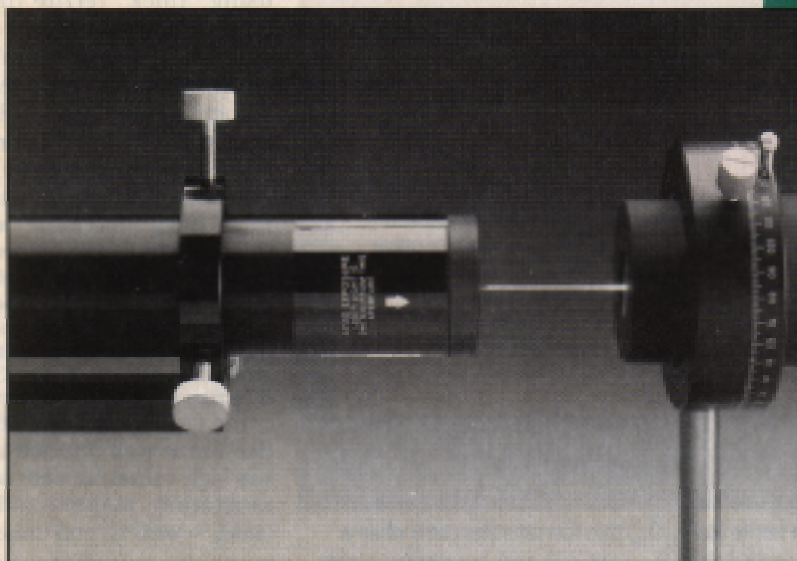
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netocrystalline anisotropy field along the c-axis, however, the film requires a large externally applied magnetic field to saturate in the film plane. In addition, the ferrimagnetic resonance (FMR) line width ( $\Delta H$ ) for  $\text{BaFe}_{12}\text{O}_{19}$  is as narrow as the line width of bulk single-crystal  $\text{BaFe}_{12}\text{O}_{19}$ , indicating relatively small magnetic losses (see Fig. 4, inset). The dielectric losses for the film are very low. This example demonstrates the high structural and magnetic quality of ferrite films that can be achieved using PLD.

Although it has been almost 30 years since the first multicomponent thin film was produced using pulsed laser deposition, the power of the technique has only been realized within the last few

The overwhelming potential of high-temperature superconductive electronics catalyzed the breakthrough of pulsed laser deposition in reproducible ceramic thin-film production,

years. The rapid growth of the field was catalyzed by the discovery of high-temperature superconductivity and the difficulties encountered in trying to fabricate devices from these materials using more conventional physical vapor deposition techniques. Following the successful growth of HTS films by PLD, the application of the technique has expanded enormously to include a broad spectrum of complex, multicomponent materials.

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